

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B01J 31/12, 31/14, 31/02, C07C 67/08, C08G 63/82</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/28033</b> <b>(43) International Publication Date:</b> 10 June 1999 (10.06.99)
<b>(21) International Application Number:</b> PCT/GB98/03448 <b>(22) International Filing Date:</b> 16 November 1998 (16.11.98)  <b>(30) Priority Data:</b> 9725419.7                      2 December 1997 (02.12.97)                      GB  <b>(71) Applicant (for all designated States except US):</b> TIOXIDE SPECIALTIES LIMITED [GB/GB]; Lincoln House, 137-143 Hammersmith Road, London W14 0QL (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> RIDLAND, John [GB/GB]; 12 Oatlands Way, Durham, County Durham DH1 5GL (GB). HEPPLEWHITE, Iain, Wesley [GB/GB]; 28 Rievaulx Avenue, Billingham, Teesside TS23 2BL (GB).  <b>(74) Agents:</b> JACKSON, John, Derek et al.; ICI Group Intellectual Property, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ESTERIFICATION CATALYSTS  <b>(57) Abstract</b>  An organometallic compound suitable for use as a catalyst for the preparation of an ester comprises the reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and a base. A process for the preparation of an ester comprises carrying out an esterification reaction in the presence of the catalyst. In a further embodiment the organometallic compound suitable for use as a catalyst in an esterification process comprises the reaction product of, in addition, a 2-hydroxy carboxylic acid.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

### ESTERIFICATION CATALYSTS

The invention concerns esterification catalysts and in particular esterification catalysts which comprise novel organotitanium, organozirconium or organoaluminium compounds.

5 Organotitanium compounds and, in particular, titanium alkoxides or orthoesters are known as catalysts for esterification processes. During the esterification, these compounds are frequently converted to insoluble compounds of titanium which result in a hazy product. The presence of a haze is a particular disadvantage in polyesters which have a high viscosity and/or high  
10 melting point and are therefore difficult to filter. Furthermore, many organotitanium compounds which are effective catalysts in the manufacture of polyesters such as polyethylene terephthalate are known to produce unacceptable yellowing in the final polymer. Our co-pending application, published as GB 2 314 081 relates to an esterification process in which these  
15 problems are partially solved but there is still a need for a catalyst which induces little or no yellowing in a polyester produced using the catalyst.

It is an object of the present invention to provide an improved catalyst for a process for preparing esters.

According to the invention, an organometallic compound suitable for use  
20 as a catalyst for the preparation of an ester comprises the reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and a base.

Also according to the invention, a process for the preparation of an ester  
25 comprises carrying out an esterification reaction in the presence of a catalyst comprising the reaction product of an orthoester or condensed orthoester of

titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and a base.

In a further embodiment the organometallic compound suitable for use as a catalyst in an esterification process comprises the reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group, a base and a 2-hydroxy carboxylic acid.

The organometallic compound of the invention is the reaction product of a titanium, zirconium or aluminium orthoester or condensed orthoester, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and a base. Preferably, the orthoester has the formula  $M(OR)_4$  or  $Al(OR)_3$  where M is titanium or zirconium and R is an alkyl group. More preferably R contains 1 to 6 carbon atoms and particularly suitable orthoesters include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetra-n-propoxy zirconium, tetra-n-butoxy zirconium and tetra-iso-butoxy aluminium.

The condensed orthoesters suitable for preparing the compounds of this invention are typically prepared by careful hydrolysis of titanium, zirconium or aluminium orthoesters. Titanium or zirconium condensed orthoesters are frequently represented by the formula



in which  $R^1$  represents an alkyl group and M represents titanium or zirconium. Preferably, n is less than 20 and more preferably is less than 10. Preferably,  $R^1$  contains 1 to 12 carbon atoms, more preferably,  $R^1$  contains 1 to 6 carbon atoms

and useful condensed orthoesters include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

Preferably, the alcohol containing at least two hydroxyl groups is a dihydric alcohol and can be a 1,2-diol such as 1,2-ethanediol or 1,2-propanediol, a 1,3-diol such as 1,3-propanediol, a 1,4-diol such as 1,4-butanediol, a diol containing non-terminal hydroxyl groups such as 2-methyl-2,4-pentanediol or a dihydric alcohol containing a longer chain such as diethylene glycol or a polyethylene glycol. Preferred dihydric alcohols are 1,2-ethanediol and diethylene glycol. The organometallic compound can also be prepared from a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol.

Preferably, the organometallic compound useful as a catalyst is prepared by reacting a dihydric alcohol with an orthoester or condensed orthoester in a ratio of from 1 to 16 moles of dihydric alcohol to each mole of titanium, zirconium or aluminium. More preferably, the reaction product contains 2 to 12 moles of dihydric alcohol per mole of titanium, zirconium or aluminium and most preferably 4 to 8 moles dihydric alcohol per mole of titanium, zirconium or aluminium.

The organophosphorus compound which contains at least one P-OH group can be selected from a number of organophosphorus compounds including phosphates, pyrophosphates, phosphonates, phosphinates and phosphites.

Preferably, the organophosphorus compound is a substituted or unsubstituted alkyl phosphate, a substituted or unsubstituted aryl phosphate or a phosphate of an alkylaryl glycol ether or an alkyl glycol ether. Preferred compounds include monoalkyl acid phosphates and dialkyl acid phosphates and mixtures of these. Particularly convenient organophosphorus compounds are the

compounds commercially available as alkyl acid phosphates and containing, principally, a mixture of mono- and di-alkyl phosphate esters. When an alkyl phosphate is used, the organic group preferably contains up to 20 carbon atoms, more preferably up to 8 carbon atoms and, most preferably, up to 6 carbon atoms. When alkylaryl or alkyl glycol ether phosphates are used the carbon chain length is preferably up to 18 carbon atoms and, more preferably, 6 to 12 carbon atoms. Particularly preferred organophosphorus compounds include butyl acid phosphate, polyethylene glycol phosphates and aryl polyethylene glycol phosphates.

10       The amount of organophosphorus compound present in the reaction product of the invention is usually in the range 0.1 to 4.0 mole of phosphorus to 1 mole of metal (titanium, zirconium or aluminium), preferably in the range 0.1 to 2.0 mole phosphorus to 1 mole metal and most preferably in the range 0.1 to 1.0 mole phosphorus to 1 mole metal.

15       A base is also used in preparing the reaction product of the invention. The base is generally an inorganic base and suitable bases include sodium hydroxide, potassium hydroxide and ammonium hydroxide, but organic bases such as tetrabutyl ammonium hydroxide or choline hydroxide [trimethyl-(2-hydroxyethyl)ammonium hydroxide] can also be used. Usually, the amount of  
20 base used is in the range 0.1 to 4.0 mole base per mole of metal (titanium, zirconium or aluminium). The preferred amount is in the range 0.1 to 2.0 mole base per mole of metal and, frequently, the amount of base present is in the range 0.1 to 1.0 mole base per mole of titanium, zirconium or aluminium.

When 2-hydroxy carboxylic acids are used to prepare the products of the  
25 invention, preferred acids used include lactic acid, citric acid, malic acid and tartaric acid. Some suitable acids are supplied as hydrates or as aqueous

mixtures and can be used in this form. When a 2-hydroxy acid is present, the preferred molar ratio of acid to titanium, zirconium or aluminium in the reaction product is 0.5 to 4 moles per mole of titanium, zirconium or aluminium. More preferably the catalyst contains 1.0 to 3.5 moles of 2-hydroxy acid per mole of  
5 titanium, zirconium or aluminium.

The organometallic compound can be prepared by mixing the components (orthoester or condensed orthoester, alcohol containing at least two hydroxyl groups, organophosphorus compound and base) with removal, if desired, of any by-product, (e.g. isopropyl alcohol when the orthoester is  
10 tetraisopropoxytitanium), at any appropriate stage. In one preferred method the orthoester or condensed orthoester and a dihydric alcohol are mixed and, subsequently, a base is added, followed by the organophosphorus compound. When a 2-hydroxy carboxylic acid is also present in the reaction product, this is usually added to the orthoester or condensed orthoester before the  
15 organophosphorus compound is added. Alternatively, all or part of the 2-hydroxy carboxylic acid can be neutralised with the base and the resulting salt added to the other components of the reaction mixture, including, if desired, a further portion of the base.

The esterification reaction of the process of the invention can be any  
20 reaction by which an ester is produced. The reaction may be (i) a direct esterification in which a carboxylic acid or its anhydride and an alcohol react to form an ester or (ii) a transesterification (alcoholysis) in which a first alcohol reacts with a first ester to produce an ester of the first alcohol and a second alcohol produced by cleavage of the first ester or (iii) a transesterification  
25 reaction in which two esters are reacted to form two different esters by exchange of alkoxy radicals. Direct esterification or transesterification can be used in the

production of polymeric esters and a preferred process of the invention comprises a polyesterification process. Many carboxylic acids and anhydrides can be used in direct esterification including saturated and unsaturated monocarboxylic acids and anhydrides of such acids such as stearic acid, 5 isostearic acid, capric acid, caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid and rosin acids such as abietic acid, dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid and 10 pamoic acid and anhydrides of these acids and polycarboxylic acids such as trimellitic acid, citric acid, trimesic acid, pyromellitic acid and anhydrides of these acids. Alcohols frequently used for direct esterification include aliphatic straight chain and branched monohydric alcohols such as butyl, pentyl, hexyl, octyl and stearyl alcohols, dihydric alcohols such as 1,2-ethanediol, 1,3-propanediol, 15 1,4-butanediol and 1,6-hexanediol and polyhydric alcohols such as glycerol and pentaerythritol. A preferred process of the invention comprises reacting 2-ethylhexanol with phthalic anhydride to form bis(2-ethylhexyl)phthalate.

The esters employed in an alcoholysis reaction are generally the lower homologues such as methyl, ethyl and propyl esters since, during the 20 esterification reaction, it is usual to eliminate the displaced alcohol by distillation.

These lower homologue esters of the acids suitable for direct esterification are suitable for use in the transesterification process according to the invention. Frequently (meth)acrylate esters of longer chain alcohols are produced by alcoholysis of esters such as methyl acrylate, methyl methacrylate, ethyl acrylate 25 and ethyl methacrylate. Typical alcohols used in alcoholysis reactions include butyl, hexyl, n-octyl and 2-ethyl hexyl alcohols and substituted alcohols such as



dimethylaminoethanol.

When the esterification reaction is a transesterification between two esters, generally the esters will be selected so as to produce a volatile product ester which can be removed by distillation.

5 As mentioned hereinbefore, polymeric esters can be produced by processes involving direct esterification or transesterification and a particularly preferred embodiment of the esterification process of the invention is a polyesterification reaction in the presence of the catalyst described hereinbefore. In a polyesterification reaction polybasic acids or esters of polybasic acids are  
10 usually reacted with polyhydric alcohols to produce a polymeric ester. Linear polyesters are often produced from dibasic acids such as those mentioned hereinbefore or esters of said dibasic acids and dihydric alcohols. Preferred polyesterification reactions according to the invention include the reaction of terephthalic acid or dimethyl terephthalate with 1,2-ethanediol (ethylene glycol)  
15 to produce polyethylene terephthalate or with 1,4-butanediol (butylene glycol) to produce polybutylene terephthalate or reaction of naphthalene dicarboxylic acid with 1,2-ethanediol to produce polyethylene naphthalenate. Other glycols such as 1,3-propanediol, 1,6-hexanediol and polyhydric alcohols such as glycerol, trimethylolpropane and pentaerythritol are also suitable for preparing polyesters.

20 The esterification reaction of the invention can be carried out using any appropriate, known technique for an esterification reaction.

A typical process for the preparation of polyethylene terephthalate comprises two stages. In the first stage terephthalic acid or dimethyl terephthalate is reacted with 1,2-ethanediol to form a prepolymer and the  
25 by-product water or methanol is removed. The prepolymer is subsequently heated in a second stage to remove 1,2-ethanediol and form a long chain

polymer. Either or both these stages may comprise an esterification process according to this invention.

In direct esterification the acid or anhydride and an excess of alcohol are typically heated, if necessary in a solvent, in the presence of the catalyst. Water  
5 is a by-product of the reaction and this is removed, as an azeotrope with a boiling mixture of solvent and/or alcohol. Generally, the solvent and/or alcohol mixture which is condensed is immiscible with water which is therefore separated before solvent and/or alcohol are returned to the reaction vessel. When reaction is complete the excess alcohol and, when used, solvent are  
10 evaporated. In view of the fact that the catalysts of the invention do not normally form insoluble species, it is not generally necessary to remove them from the reaction mixture, as is frequently necessary with conventional catalysts. A typical direct esterification reaction is the preparation of bis(2-ethylhexyl) phthalate which is prepared by mixing phthalic anhydride and 2-ethyl hexanol. An initial  
15 reaction to form a monoester is fast but the subsequent conversion of the monoester to diester is carried out by refluxing in the presence of the catalyst at a temperature of 180-200°C until all the water has been removed. Subsequently the excess alcohol is removed.

In an alcoholysis reaction, the ester, first alcohol and catalyst are mixed  
20 and, generally, the product alcohol (second alcohol) is removed by distillation often as an azeotrope with the ester. Frequently it is necessary to fractionate the vapour mixture produced from the alcoholysis in order to ensure that the second alcohol is separated effectively without significant loss of product ester or first alcohol. The conditions under which alcoholysis reactions are carried out  
25 depend principally upon the components of the reaction and generally components are heated to the boiling point of the mixture used.

A preferred process of the invention is the preparation of polyethylene terephthalate. A typical batch production of polyethylene terephthalate is carried out by charging terephthalic acid and ethylene glycol to a reactor along with catalyst if desired and heating the contents to 260 - 270°C under a pressure of about 0.3 MPa. Reaction commences as the acid dissolves at about 230°C and water is removed. The product is transferred to a second autoclave reactor and catalyst is added, if needed. The reactor is heated to 285 - 310°C under an eventual vacuum of 100 Pa to remove ethylene glycol by-product. The molten product ester is discharged from the reactor, cooled and chipped. The chipped polyester may be then subjected to solid state polymerisation, if appropriate.

The amount of catalyst used in the esterification process of the invention generally depends upon the titanium, zirconium or aluminium content, expressed as Ti, Zr or Al, of the catalyst. Usually the amount is from 30 to 1000 parts per million (ppm) of metal on weight of product ester for direct or transesterification reactions. Preferably, the amount is from 30 to 450 ppm of metal on weight of product ester and more preferably 50 to 450 ppm of metal on weight of product ester. In polyesterification reactions the amount used is generally expressed as a proportion of the weight of product polyester and is usually from 5 to 500 ppm expressed as Ti, Zr or Al based on product polyester. Preferably the amount is from 5 to 100 ppm expressed as Ti, Zr or Al based on product polyester.

The products of this invention have been shown to be effective catalysts for producing esters and polyesters at an economical rate without leading to haze in the final product and with a reduced amount of yellowing of polyesters in comparison to known catalysts. They have also been shown to be stable against precipitation from polyester products when aqueous base or phosphoric acid is added to such products.

The invention is illustrated by the following examples.

**Preparation of Compounds for use as Catalysts**

**EXAMPLE 1**

Ethylene glycol (496.0 g, 8.00 moles) was added from a dropping funnel  
5 to stirred titanium n-butoxide (340 g, 1.00 mole) in a 1 litre fishbowl flask fitted  
with stirrer, condenser and thermometer. An aqueous solution of sodium  
hydroxide, containing 32% NaOH by weight, (125 g, 1.00 mole) was added to  
the reaction flask slowly with mixing to yield a clear pale yellow liquid. To this  
liquid was then added a polyethylene glycol phosphate having a carbon chain  
10 length of 12 carbon atoms and available commercially under the trade name  
Knapsack 194, (215.8 g, 0.55 mole of phosphorus) and the resulting mixture  
was stirred for 1 hour to produce a pale yellow liquid with a Ti content of 4.07%  
by weight.

**EXAMPLE 2**

15 The method of Example 1 was repeated with the difference that 0.28  
mole based on phosphorus (107.9 g) Knapsack 194 was added. The product  
was a pale yellow liquid with a Ti content of 4.49% by weight.

**EXAMPLE 3**

The method of Example 1 was repeated but 0.50 mole, based on  
20 phosphorus (91.0 g) commercial butyl acid phosphate (mixture of mono- and  
di-butyl acid phosphates) was used in place of the Knapsack 194. The product  
was a pale yellow liquid with a Ti content of 4.56% by weight.

**EXAMPLE 4**

The method of Example 3 was repeated except that the amount of butyl acid phosphate used was 1.00 mole based on phosphorus (182.0 g). The product was a pale yellow liquid with a Ti content of 4.20% by weight.

**5 EXAMPLE 5**

The method of Example 1 was repeated but 0.64 mole based on phosphorus (431.6g) of an aryl polyethylene glycol phosphate, sold commercially under the trade name Knapsack 123 was used in place of the Knapsack 194. The product was a pale yellow liquid with a Ti content of 3.45%  
10 by weight.

**EXAMPLE 6**

The method of Example 5 was repeated except that the amount of Knapsack 123 used was 0.32 mole based on phosphorus (215.8 g). The product was a pale yellow liquid with a Ti content of 4.08% by weight.

**15 EXAMPLE 7**

Ethylene glycol (248.0 g, 4.0 moles) was added dropwise to stirred titanium isopropoxide (142 g, 0.5 moles) in a 1 litre fishbowl flask fitted with a stirrer, thermometer and condenser. Aqueous potassium lactate (60% by weight, 213.5 g, 1.0 mole) was added from a dropping funnel to the clear solution which  
20 was then heated to 65° C under vacuum and volatile solvents were removed to yield a clear, pale yellow liquid. A portion (82.19 g, 0.1 mole Ti) was weighed into a 250 ml conical flask and commercial butyl acid phosphate (9.1 g, 0.05 moles based on phosphorus) was added from a dropping funnel with stirring. The final product was a clear, pale yellow liquid (Ti content 5.26% by weight).

**EXAMPLE 8**

Ethylene glycol (49.6 g, 0.8 moles) was added by dropping funnel to stirred titanium n-butoxide (34.0 g, 0.1 mole) in a 250 ml conical flask. An aqueous solution of sodium hydroxide containing 32% NaOH by weight (12.5 g, 0.1 mole) was added followed by a polyethylene glycol phosphate having a carbon chain length of 12 and available commercially under the trade name Knapsack 122 (32.3 g, 0.05 moles based on phosphorus). The resulting product was a white solid having a Ti content of 3.74% by weight.

**EXAMPLE 9**

10 Ethylene glycol (49.6 g, 0.8 mole) was added by dropping funnel to stirred titanium n-butoxide (34.0 g, 0.1 mole) in a 250 ml conical flask. An aqueous solution of sodium hydroxide containing 32% NaOH by weight (12.5 g, 0.1 mole) was added followed by dibutyl phosphate (10.5 g, 0.05 mole). The resulting product was a hazy liquid having a measured Ti content of 4.56% by weight.

**EXAMPLE 10**

20 Monoethylene glycol (49.6 g, 0.8 mole) was added by dropping funnel to stirred condensed titanium alkoxide known as polybutyl titanate (Tilcom® PBT) (Ti content 20.0% by wt) (24.2 g, 0.10 moles Ti) in a 250 ml conical flask. An aqueous solution of sodium hydroxide containing 32% NaOH by weight (12.5 g, 0.1 mole) was added followed by a commercial butyl phosphate (9.1 g, 0.05mole based on phosphorus). The resulting product was a white solid having a Ti content of 5.03% by weight.

**EXAMPLE 11**

Diethylene glycol (848 g, 8.0 moles) was added by dropping funnel to stirred zirconium n-propoxide (Tilcom® NPZ) (445 g, 1.0 mole Zr) in a 2 litre-flask. A portion of this solution (129.3 g, 0.1 moles Zr) was weighed into a 250 ml conical flask and an aqueous solution containing 45% choline hydroxide by weight (13.45 g, 0.05 moles) was added followed by a commercial butyl phosphate (9.1 g, 0.05 moles based on phosphorus). The resulting product was a clear yellow solution having a Zr content of 6.01% by weight.

**EXAMPLE 12**

10 Diethylene glycol (84.8 g, 0.8 mole) was added by dropping funnel to stirred aluminium sec-butoxide (24.6 g, 0.1 mole) in a 250 ml conical flask. An aqueous solution of sodium hydroxide containing 32% NaOH by weight (12.5 g, 0.1 mole) was added followed by a commercial butyl phosphate (9.1 g, 0.05mole based on phosphorus). The resulting product was a clear solid gel having an Al  
15 content of 2.06% by weight.

**EXAMPLE 13**

Ethylene glycol (24.8 g, 0.4 mole) was added by dropping funnel to stirred titanium n-butoxide (34.0 g, 0.1 mole) in a 250 ml conical flask. An aqueous solution containing 45% by weight of choline hydroxide (26.93 g,  
20 0.1mole) was added followed by a commercial butyl phosphate (18.2 g, 0.1 mole based on phosphorus). The resulting product was a clear pale yellow liquid having a Ti content of 4.62% by weight.

**EXAMPLE 14**

Ethylene glycol (99.2 g, 1.6 mole) was added by dropping funnel to  
25 stirred titanium n-butoxide (68.1 g, 0.2 mole) in a 250 ml conical flask. An aqueous solution of sodium hydroxide containing 32% by weight NaOH (25.0 g,

0.2 mole) was added followed by commercial butyl phosphate (18.2 g, 0.1 mole). The resulting clear liquid product was transferred to a 500 ml rotary evaporator flask and solvents were removed under vacuum at 95° C to yield a hazy liquid having a Ti content of 10.54% by weight.

5

### Esterification

#### EXAMPLE 15

The products of Examples 1, 3, 5 and 7 were tested at a concentration of 170 ppm Ti as catalysts for the preparation of bis(2-ethylhexyl phthalate). Titanium tetra-isopropoxide  $[Ti(OPr^i)_4]$  was used as a comparative catalyst.

10 The apparatus was a 1-litre, 4-necked round-bottomed flask fitted with a thermometer, rubber seal, a tube dipping below the surface of the reactants and a Dean and Stark apparatus. The equipment was operated under reduced pressure using an oil vacuum pump connected to two water condensers fitted above the Dean and Stark apparatus. The dip tube in the flask was connected  
15 to a supply of oxygen-free nitrogen. This provided a nitrogen bleed to aid the removal of water during the reaction.

1.0 mole (148 g) phthalic anhydride was added to 2.42 moles (315 g) 2-ethylhexanol. The mixture was heated to dissolve the phthalic anhydride and the nitrogen flow started.

20 A weighed amount of catalyst was added to the reaction flask in a porcelain boat before heating the mixture, except for  $Ti(OPr^i)_4$  which was added as a solution in 2-ethylhexanol via the rubber seal with a syringe, below the surface of the reactants. The reaction mixture was heated to and maintained at a vigorous reflux at 200°C by suitable adjustment of the heating rate and  
25 vacuum. The water produced was removed substantially as quickly as it was



formed and collected in the Dean and Stark apparatus.

The progress of the reaction was followed by withdrawing samples at intervals by means of a syringe fitted with a 30 cm needle inserted through the rubber seal. Each sample was added to a known weight (approximately 100 g) of cold alcohol to quench the reaction, weighed and titrated against standard potassium hydroxide solution in ethanol using bromophenol blue as indicator. The results were used to calculate the amount of unreacted half-ester present.

The reaction was continued for a total of 160 minutes.

The results are given in Table 1 below:

10

**TABLE 1**

Catalyst	Product Colour <sup>1</sup>	Product Clarity	% Conversion
Ti(OPr <sup>i</sup> ) <sub>4</sub>	85	Hazy	99.95
Example 1	70	Clear	98.59
Example 3	60	Clear	96.43
Example 5	70	Clear	97.64
Example 7	80	Clear	93.54

<sup>1</sup>. Hazen units. Colour of final reaction mixture.

#### **EXAMPLE 16**

The products of Examples 3, 5 and 8 to 14 were tested at a concentration of 164 ppm Ti or Al or 340 ppm Zr based on reactants as catalysts for the preparation of monoethyleneglycol benzoate. Titanium isopropoxide [Ti(OPr<sup>i</sup>)<sub>4</sub>] and antimony oxide were used as comparative examples.

The apparatus was a 1-litre, 4-necked round bottom flask fitted with thermometer, rubber seal, dip tube below the surface of reactants and Dean and

Stark apparatus. A glass column (30 cm) containing glass beads was attached between the reaction flask and Dean and Stark apparatus. The equipment was operated under vacuum using an oil vacuum pump connected to a water condenser above the Dean and Stark apparatus. The dip tube was connected to  
5 a supply of oxygen-free nitrogen and provided a nitrogen bleed to aid the removal of water during the reaction.

0.5 mole (61.06 g) benzoic acid was added to 10 moles (620 g) monoethylene glycol. The excess of glycol was used to prevent benzoic acid sublimation and to minimise polycondensation reactions. The catalysts were  
10 added as solutions or suspensions in the monoethyleneglycol to ensure good dispersion. The mixture was heated to dissolve the benzoic acid and the nitrogen flow started. The temperature was raised to 180° C and after 5 minutes a slight vacuum was applied and the temperature raised to 200° C. Distillation of the water/monoethylene glycol commenced at about 150° C and the reactions  
15 were maintained at a vigorous reflux at 190 to 193° C by suitable adjustment of heating rate and vacuum. The water produced was removed with monoethyleneglycol and collected via the Dean and Stark apparatus.

Progress of the reaction was followed by withdrawing samples at intervals by means of a syringe fitted with a 30 cm needle inserted through the  
20 rubber seal. Each sample was added to a known weight (approximately 100 g) of cold alcohol to quench the reaction, weighed and titrated against standard potassium hydroxide solution in ethanol using bromophenol blue as indicator. The results of acid value (AV) were used to calculate the percentage conversion to benzoate ester. The reactions were each monitored for a total of 180 minutes.  
25 The results are given in Table 2 below.

**TABLE 2**

Catalyst	% Conversion				Ester Colour
	90 min.	120 min.	150 min.	180 min.	
Sb oxide*	46.09	53.05	61.05	66.16	pale yellow
Ti(OPr) <sub>4</sub>	70.63	81.84	99.67	99.39	colourless
Example 8	92.83	98.59	99.39	99.53	colourless
Example 9	96.60	99.27	99.62	99.61	colourless
Example 10	94.91	97.42	98.03	98.52	colourless
Example 11	45.93	50.40	50.97	54.60	white/cloudy
Example 12	32.09	38.50	44.50	50.44	white/cloudy
Example 13	97.61	98.43	99.76	99.87	colourless
Example 14	95.75	98.27	99.48	99.66	colourless
Example 5	97.23	97.54	98.04	99.60	colourless
Example 3	98.56	99.01	99.10	99.78	colourless

\* Amspec Select Antimony Oxide (3%wt/wt monoethylene glycol) at 164 ppm Sb.

After the reaction flask had cooled, a sample was removed for gas chromatographic (GC) analysis. It was found that different catalysts produced 5 varying proportions of the products. The products formed were ethyleneglycol monobenzoate (EGMB), ethyleneglycol dibenzoate (EGDB), diethyleneglycol (DEG), diethyleneglycol monobenzoate (DEGMB) and diethylene glycol dibenzoate (DEGDB). The proportions (by area % from GC) are reported in Table 3.

**TABLE 3**

Catalyst	EGMB	EGDB	DEG	DEGMB	DEGDB
Sb oxide*	6.67	0.72	0.48	2.75	-
Ti(OPr) <sub>4</sub>	1.71	17.26	0.46	0.47	3.95
Example 8	1.93	12.89	ca 0.04	0.08	0.71
Example 9	1.94	12.88	ca 0.04	0.24	0.48
Example 10	1.98	14.58	ca 0.08	0.26	0.30
Example 11	1.38	3.93	0.53	0.45	2.36
Example 12 <sup>#</sup>	0.91	4.01	0.70	0.41	1.39
Example 13 <sup>#</sup>	2.16	15.62	0.15	0.27	0.77
Example 14	1.79	19.87	ca 0.07	0.30	0.91
Example 5	3.02	25.60	0.28	0.24	1.28
Example 3	2.61	19.10	0.1	0.21	0.91

\* Amspec Select Antimony Oxide (3%wt/wt monoethylene glycol) at 164 ppm Sb.

<sup>#</sup>Analysis of supernatant liquor.

The results demonstrate that the catalysts of the invention are effective  
 5 for the esterification reaction of benzoate esters and produce products with  
 lower levels of DEG by-product than antimony oxide or conventional titanium  
 catalysts.

#### **EXAMPLE 17**

A polycondensation reaction was carried out in a mechanically-stirred  
 10 300 ml glass vessel fitted with side arm and cold trap for collection of  
 monoethyleneglycol. A thermostatically controlled ceramic heating element was  
 used to provide heat and an oil vacuum pump was connected to the cold trap. A  
 nitrogen blanket was provided via a connection to the cold trap.

Polyethylene terephthalate was prepared from (hydroxyethyl)terephthalate polymer precursors supplied by ICI Polyesters. Two samples were used; sample A was a short chain polymer containing approximately 4 ethylene terephthalate repeating units whilst sample B was technically pure bis(hydroxyethyl)terephthalate. Sample A also contained approximately 5 mol% acid end groups.

100 g of (hydroxy)terephthalate polymer precursor was placed in the reaction flask under a nitrogen flow, followed by a dilute solution of catalyst (Ti added at 30 ppm) in monoethyleneglycol. This was heated with stirring to 250° C for 20-25 minutes at which point a stabiliser (phosphoric acid, 100 ppm) and cobalt acetate tetrahydrate (250 ppm) were added, again as solutions in monoethyleneglycol. The nitrogen flow was stopped and vacuum applied steadily to 100 Pa. After 20-25 minutes the temperature was increased steadily from 250° C to 290° C. The power consumption of the electrical stirrer increased with the viscosity of the polymer and the stirrer revolutions dropped. The revolutions were monitored until a predetermined value for the peripheral speed of the agitator tip (15km/h) was reached at which point the vacuum was broken with nitrogen and the molten polymer discharged and quenched into cold water. It was then dried for 10-14 hours at 50° C in a vacuum oven.

20 The colour of the polymer was measured using a Colorgard System 2000 Colorimeter. Common models to use for colour expression are the Hunter Lh, ah and bh or Cielab L\*, a\* and b\* scales where the b-value in both describe yellowness. The yellowness of the polymer increases with b-value.

The polymer molecular weights were measured by Gel Permeation  
25 Chromatography (GPC).

The results are given in Table 4.

**TABLE 4**

Catalyst	Monomer Sample	Reaction Time (Minutes)	Colour (b* value)	Colour (bh value)	Molecular Weight (Mn)
Sb oxide*	A	195	6	5.32	19,330
Ti(OPr) <sub>4</sub>	A	110	6.7	5.37	16,290
Example 5	A	140	3.39	2.78	11,480
Example 3	A	145	3.34	2.57	14,130
Sb oxide*	B	135	0.71	0.56	19,550
Ti(OPr) <sub>4</sub>	B	115	9.06	6.67	15,190
Example 5	B	80	5.93	4.63	12,770
Example 3	B	100	4.05	2.9	15,420
Example 10	B	100	8.65	6.30	NA
Example 13	B	95	4.47	3.56	NA

\* Antimony oxide Catalyst Grade from SICA added at 250 ppm Sb.

NA - not available.

These results indicate that the catalysts of the invention are active for the  
5 preparation of polyethylene terephthalate and are capable of producing polymer  
with lower yellowness values than conventional titanium-based catalysts.

#### **EXAMPLE 18**

It has been postulated that one mechanism causing discolouration when  
titanium catalysts are used to prepare polyethylene terephthalate is interaction of  
10 the catalyst with a thermal decomposition product of polyethylene terephthalate.  
Catalysts of Examples 1 to 7 were assessed by mixing with one such  
decomposition product, diethyldihydroxy terephthalate (DEDHT) in toluene. The

standard catalyst, titanium tetra-isopropoxide  $[\text{Ti}(\text{OPr}^i)_4]$  was used for comparison and was added to 0.4 g DEDHT in 10 ml toluene. The catalysts of Examples 1 to 7 were added to DEDHT/toluene solution of a similar concentration in an amount sufficient to produce the same Ti concentration in the mixture and the colour of each of the mixtures was determined using a LICO 200 spectrophotometer in 11 ml glass cuvettes. The results are given in Table 5.

**TABLE 5**

Catalyst	Colour (Gardner units)
None	6
$\text{Ti}(\text{OPr}^i)_4$	11.9
Example 1	6
Example 2	8.5
Example 3	5.5
Example 4	5.5
Example 5	5.5
Example 6	8.5
Example 7	7

**CLAIMS**

1. An organometallic compound suitable for use as a catalyst for the preparation of an ester comprising the reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and a base.

2. An organometallic compound according to claim 1 comprising the reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group, a base and a 2-hydroxy carboxylic acid.

3. An organometallic compound according to claim 2 characterised in that the 2-hydroxy acid is lactic acid, citric acid, malic acid or tartaric acid.

4. An organometallic compound according to any one of the preceding claims characterised in that the orthoester has the formula  $M(OR)_4$  or  $Al(OR)_3$  where M is titanium or zirconium and R is an alkyl group containing from 1 to 6 carbon atoms.

5. An organometallic compound according to any one of claims 1, 2 and 3 characterised in that the condensed orthoester has a structure which can be represented by the formula,  $R^1O[M(OR^1)_2O]_nR^1$  where M is titanium or zirconium,  $R^1$  is an alkyl group containing 1 to 6 carbon atoms and n is less than 20.

6. An organometallic compound according to any one of the preceding claims characterised in that the alcohol containing at least two hydroxyl groups is 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-2,4-pentanediol, diethylene glycol, polyethylene glycol, glycerol, trimethylolpropane or pentaerythritol.



7. An organometallic compound according to any one of the preceding claims characterised in that the reaction product is prepared by reacting a dihydric alcohol with an orthoester or condensed orthoester in a ratio of from 1 to 16 moles of dihydric alcohol to each mole of titanium, zirconium or aluminium.

5 8. An organometallic compound according to any one of the preceding claims characterised in that the organophosphorus compound is a phosphate, a pyrophosphate, a phosphonate, a phosphinate or a phosphite.

9. An organometallic compound according to any one of the preceding claims characterised in that the organophosphorus compound is a substituted or  
10 unsubstituted alkyl phosphate, a substituted or unsubstituted aryl phosphate or a phosphate of an alkylaryl glycol ether or an alkyl glycol ether.

10. An organometallic compound according to any one of the preceding claims characterised in that the organophosphorus compound is an alkyl phosphate in which the organic group contains up to 20 carbon atoms.

15 11. An organometallic compound according to any one of claims 1 to 9 characterised in that the organophosphorus compound is a phosphate of an alkylaryl glycol ether or an alkyl glycol ether having a carbon chain length up to 18 carbon atoms.

12. An organometallic compound according to any one of the preceding  
20 claims characterised in that the organophosphorus compound is present in an amount in the range 0.1 to 4.0 mole of phosphorus to 1 mole of titanium, zirconium or aluminium.

13. An organometallic compound according to any one of the preceding claims characterised in that the base is present in an amount in the range 0.1 to  
25 4.0 mole of base to 1 mole of titanium, zirconium or aluminium.

14. An organometallic compound according to any one of claims 2 to 13 characterised in that the 2-hydroxy acid is present in an amount in the range 0.5 to 4 mole acid to 1 mole of titanium, zirconium or aluminium.

15. A process for the preparation of an ester comprising carrying out an esterification reaction in the presence of a catalyst comprising the reaction product of an orthoester or condensed orthoester of titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and a base.

16. A process according to claim 15 characterised in that the esterification reaction comprises reaction of an alcohol with stearic acid, isostearic acid, capric acid, caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid, a rosin acid, abietic acid, phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid, pamoic acid, trimellitic acid, citric acid, trimesic acid or pyromellitic acid.

17. A process according to claim 15 characterised in that the esterification reaction comprises reaction of an alcohol with an anhydride of a dicarboxylic acid or a tricarboxylic acid.

18. A process according to claim 15 characterised in that the esterification reaction comprises reaction of a methyl ester, an ethyl ester or a propyl ester of acrylic acid or methacrylic acid with an alcohol.

19. A process according to claim 15 characterised in that the esterification reaction comprises reaction of two esters to produce two different esters by exchange of alkoxy groups.

20. A process according to claim 15 characterised in that the esterification reaction comprises a polyesterification comprising the reaction of terephthalic acid, dimethyl terephthalate or naphthalene dicarboxylic acid with 1,2-ethanediol, 1,4-butanediol, 1,3-propanediol, 1,6-hexanediol, trimethylol-  
5 propane or pentaerythritol.

21. A process according to any one of claims 15 to 19 characterised in that the catalyst is present in an amount in the range 30 to 1000 parts per million calculated as parts by weight titanium, zirconium or aluminium with respect to weight of product ester.

10 22. A process according to claim 15 or 21 characterised in that the esterification reaction is a polyesterification and the catalyst is present in an amount in the range 5 to 500 parts per million calculated as parts by weight titanium, zirconium or aluminium with respect to weight of product polyester.

# INTERNATIONAL SEARCH REPORT

Inter national Application No  
PCT/GB 98/03448

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J31/12 B01J31/14 B01J31/02 C07C67/08 C08G63/82

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07C C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP 0 816 354 A (BAYER AG) 7 January 1998 see page 8, line 35 - page 9, line 55 see examples 3-5	1, 4
X	WO 96 37534 A (FISCHER KARL IND GMBH ;HAGEN RAINER (DE); SCHAAF ECKEHART (DE); ZI) 28 November 1996 see example 5 see page 5, line 27 - line 31	1, 4, 6, 8-10, 15, 20
A, P	GB 2 314 081 A (TIOXIDE SPECIALTIES LTD) 17 December 1997 cited in the application	
A	DE 24 34 213 A (ICI LTD) 6 February 1975	
A	US 4 072 631 A (VOGT HERWART CURT ET AL) 7 February 1978	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

Date of the actual completion of the international search

26 February 1999

Date of making of the international search report

08/03/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3018

Authorized officer

Thion, M

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/GB 98/03448

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0816354 A	07-01-1998	DE 19625265 A	02-01-1998
		DE 19629462 A	29-01-1998
		JP 10059957 A	03-03-1998
		US 5861107 A	19-01-1999
WO 9637534 A	28-11-1996	DE 19518943 A	28-11-1996
		CN 1190411 A	12-08-1998
		EP 0827518 A	11-03-1998
GB 2314081 A	17-12-1997	AU 2363597 A	18-12-1997
		BR 9703577 A	10-11-1998
		CA 2207111 A	11-12-1997
		CZ 9701762 A	13-05-1998
		EP 0812818 A	17-12-1997
		HU 9701024 A	02-03-1998
		JP 10081646 A	31-03-1998
		NO 972645 A	12-12-1997
		PL 320469 A	22-12-1997
		US 5866710 A	02-02-1999
DE 2434213 A	06-02-1975	GB 1421972 A	21-01-1976
		AU 7115274 A	15-01-1976
		FR 2237924 A	14-02-1975
		JP 50054692 A	14-05-1975
		JP 53008352 B	28-03-1978
		NL 7409320 A	20-01-1975
		US 3965071 A	22-06-1976
US 4072631 A	07-02-1978	NONE	